

O. BROTZEN

A GRAPH FOR THE CHEMICAL
DIAGNOSIS OF ROCKS



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ABSTRACT

The chemical composition of rocks is used to illuminate the original nature of highly metamorphic rocks, as well as the role of subsequent alterations. For this purpose each composition is viewed in relation to known effects of common rock-forming processes by means of a special triangular diagram, showing total composition, and expressing ten separate variables. These often permit quantification of the effects of weathering, sorting, and igneous fractionation. Typical trends are exemplified by a selection of well known non-metamorphic rocks. This suggests diagnostic features for tholeiitic and more alkaline igneous rocks, and for sediments of the arkose, graywacke, argillite and marl types. Diagnosis is illustrated by application to groups of leptites, gneisses and greenstones, discussing their original nature and the possible role of granitization, albitization and alkali metasomatism in these rocks.

Some general aspects of the chemical diagnosis of rocks are also discussed, and it is concluded that the individual major elements are not optimal variables for this purpose. Instead it appears advantageous to break down the contents of elements such as Si and Al into parts with different geochemical functions, and to join others into groups which express their geochemical coherence and their tendency to proxy for each other in related fractionational processes.

Statement of problem

Chemical diagnosis of rocks is sometimes compared to locating points in multi-dimensional chemical space, each point representing a particular composition, and each chemical element representing one separate dimension. This produces highly complex models calling for computers to classify rocks by various statistical tests defining rocks as clusters of compositional points. Location of points or clusters in such models may serve the description, identification, comparison and retrieval of rock-compositions, but does not in itself imply any geological or geochemical diagnosis. This can only be achieved by putting the unknown in relation to known compositions and trends, as was illustrated by a pilot test with a simplified radial model some years ago (O. Brotzen 1967). Even so the evaluation of residual differences between the unknown sample and the closest type-rocks in the system of reference often causes irritating ambiguity in actual work.

Unfortunately a number of fundamental difficulties affect such multidimensional models. Many rocks do not form more or less isometric clusters, but represent members, delimited according to convenience in petrographical work, of long and complex evolutionary series, which even may cross the boundaries between major divisions of current petrological classification. Rocks, transitional between the igneous and sedimentary divisions are, for instance, often met with in mixed volcanic – sedimentary environments, in cases of hybridization and anatexis, and in regolithic zones between igneous basements and their sedimentary cover. The recognition of such lineages in multidimensional chemical space has so far been unsuccessful.

This reflects the fact that the major elements are not independent variables in rocks. Therefore they cannot be treated as separate dimensions. On the contrary, much chemical variation is brought about by stoichiometric combinations of the major elements, and even more complex relations occur. Ca and Mg, for instance, frequently reflect the variation of a distinct carbonate fraction in rocks, but within this fraction they tend to replace each other, and hence to be negatively correlated. Furthermore individual elements may enter more than one lithochemically significant variable. Finally the entire variability of the major elements is limited by the general condition that the sum of all constituents is constant (cf. Chayes 1967).

All these limitations in the free variation of the individual elements reduce the number of dimensions required for descriptive purposes. Pioneer work on the definition of lithochemically diagnostic variables and their representation, by Bastin, Becke, Grubenmann, Osann and others, has been well summarized by Grubenmann and Niggli (1924). This, together with the synthesis on general fractionation trends, given by Goldschmidt, represents the starting point of the present study.

Principles

A relevant set of components can be selected by the following considerations of the main chemical effects of normal igneous and sedimentary processes:

Magmatic processes separate high-temperature phases, rich in divalent Mg and Ca, from low-temperature products richer in the univalent alkalis. This general trend is prevalent in highly silica-saturated systems as well as in subsilicic and alkaline rocks. Basically these changes may be formally reflected in the relations between MgSiO_3 plus CaSiO_3 on one hand and KAlSi_3O_8 plus $\text{NaAlSi}_3\text{O}_8$ on the other. Here CaSiO_3 also stands for that part of the anorthite molecule, whereas higher or lower silicates are reflected in a separate silica-variable. Iron in this thermal fractionation plays an intermediate role, and complications may arise from its participation in special redox reactions (cf. Osborne 1959).

Processes in aqueous environments generally result in the breakdown of magmatic and metamorphic minerals. High-temperature ferromagnesian minerals form chlorites, goethite, and similar phases. Feldspars form clays, (micas) and silica, with concurrent losses of lime and alkalis, notably soda. Thus, various Si-, Al- and Fe-rich rocks are produced, whereas Ca and Mg are precipitated as carbonates or become fixed in diagenesis. Here on one hand the carbonates and on the other a combination of free silica, iron oxides and alumina, except that contained in the feldspars, should form representative componental groups.

The "sedimentary" carbonates and the "igneous" Ca, Mg-silicates may further be combined into a joint Ca, Mg-group, which reflects common metamorphic reactions, but causes no ambiguity in the diagnosis of carbonate-bearing rocks, where the carbonate fraction can always be identified as such. As a result rock compositions can be expressed in terms of three componental groups, which all carry distinctive genetical meanings. Rocks can in this way be represented in triangular diagrams, cf. Fig. 1 and 2, where the three groups are given the following designations:

AF: nominal alkali feldspars $(\text{K,Na})\text{AlSi}_3\text{O}_8$;

CM: $(\text{Ca,Mg})\text{SiO}_3$ plus $(\text{Ca,Mg})\text{CO}_3$;

R: the rest, mainly excess silica, excess alumina, the Fe, Ti-oxides and water.

Within this general framework many lithochemically significant variables may be expressed, as will be shown later.

Graphical presentation

A quick survey of large numbers of rock-compositions may be obtained along these lines by plotting rocks in a triangular diagram, with $\text{CaO} + 1.2 \text{MgO}$ as the horizontal axis, and $5 (\text{K}_2\text{O} + 1.43 \text{Na}_2\text{O})$ as the vertical axis, all values in weight per cent, cf. Fig. 1. The horizontal axis then denotes the CM-component, (note the different scales for silicate- and carbonate rocks), whereas the alkalis represent the AF component. As can be seen in Fig. 1, which contains all the 50 compositions of supracrustal rocks given by Th. Lundqvist (1968) from the Loos-Hamra region, already this simple version of the graph may convey considerable information. It clearly differentiates between the various groups of rocks, in accordance with Lundqvist's petrological and geological grouping, even showing separate scatterfields for the acid metavolcanics and the younger Dala porphyries. It also brings out the high R-content of the meta-argillitic rocks and the variation at essentially constant R (i.e. parallel with the CM-AF side) in the basic groups, which has been found typical of magmatic fractionation.

More detailed diagnosis requires additional control of the variation within the three main components. In order to handle stoichiometric relations all contents are now expressed as cation per cent. The Mg:Ca variation within the CM-component is represented numerically as $m = 10 \text{Mg}/(\text{Mg} + \text{Ca})$, and the K:Na variation in the AF-component as $k = 10 \text{K}/(\text{K} + \text{Na})$. These numbers are placed immediately above the projection point of the rock in the CM:AF:R diagram, thereby marking its position, cf. Fig. 2. The k-number is placed at the top and the m-number, representing the important constituents of basic rocks, at the base.

The constituents of the R-component are shown in the following way:

Fe^{2+} and Fe^{3+} are indicated directly as cation percentages downward from the projection point of the rock. The manganese present in the rock may be included in Fe^{2+} .

Al' , which is the Al of the rock not included in AF, is plotted next as a vertical distance below the Fe^{3+} mark, and marked by a triangular dot. (In rare cases, e.g. peralkaline rocks, Al' is negative, and forms no part of R. Instead part of the iron is formally needed to balance the deficit in Al. This amount of Fe should therefore not be included in the R-term).

That part of Al' which would be included in a nominal anorthite component is twice the Ca percentage of the rock after the Ca contained in carbonates has been subtracted. This quantity is indicated as a vertical line downward from the Fe^{3+} mark. It can never exceed total Al' .

The remaining Al' , if any, is called Al'' and represents corundum, Al in spinel, and in Al-rich products of hydrolysis, such as clays, or the metamorphic aluminosilicates. It is left blank.

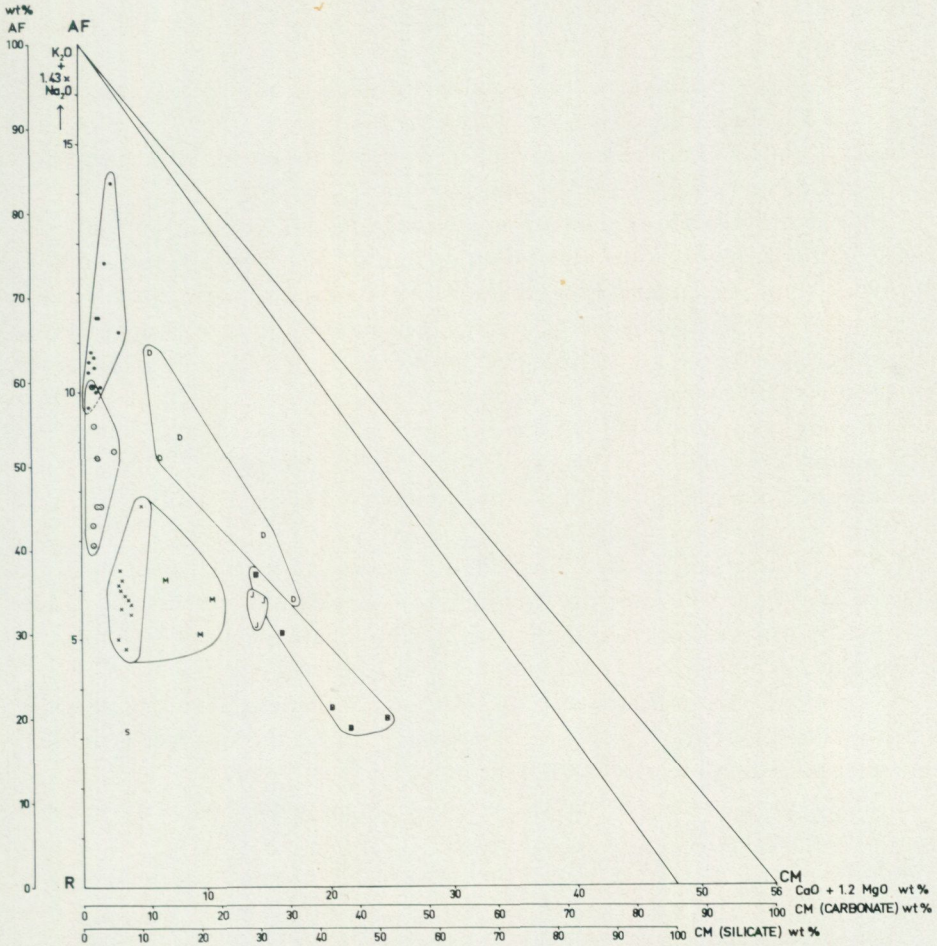


Fig. 1. CM-AF-R diagram of supracrustal rocks of the Los - Hamra region. Rock compositions and classification after Lundqvist (1968). Symbols: Crosses - meta-argillites; M - skarn-bearing meta-argillites, marly rocks; Circles - acid meta-volcanics; S - sheared and altered micaceous meta-volcanics; B - basic meta-volcanics; D - Dala porphyrites; Dots - Dala porphyries; J - Jotnian dolerites.

This as a rule ends the plotting procedure, because the remaining part of R, which is left below the Al' mark, is mainly Si', i.e. Si not contained in CM and AF. The cation percentage of carbonate carbon is indicated numerically below the lower end of Al', and Ti is shown separately at an enlarged scale below the triangular graph.

As an example of the full procedure, we may consider a graywacke listed by Pettijohn (1957, table 51,K), cf. Fig. 2. Its composition, recalculated into cation per cent, is:

Si 54.58, Al 22.08, Fe³⁺ 1.85, Fe²⁺ 2.02, Mg 3.99, Ca 6.45, Na 4.32, K 2.24, Ti 0.64, Mn 0.06, C (carbonate) 1.39.

In CM each Ca and Mg will be combined with one Si or one C, therefore:
 $CM = 2(Ca + Mg) = 2(6.45 + 3.99) = 20.88$.

In AF each K and Na will be combined with one Al and three Si, therefore:
 $AF = 5(K + Na) = 5(2.24 + 4.32) = 32.8$.

CM and AF fully locate the rock in the diagram. The R - CM and R - AF sides are therefore scaled for direct plotting of the Ca + Mg (50) and the K + Na (20) cation percentages. The position of the projection point of the rock is indicated by the base of the m number, this number in turn is obtained by $m = 10 \text{ Mg} : (\text{Mg} + \text{Ca}) = 10 \times 3.99 : (3.99 + 6.45) = 3.82$. m is indicated numerically as the nearest whole number, in this case $m = 4$. (If $m < 0.5$ it is indicated by a dot, and if $m > 9.5$ it is indicated as X.)

In a similar fashion $k = 10K : (K + Na) = 10 \times 2.24 : (2.24 + 4.32) = 3.42$. It is indicated numerically (3) above the m-number. The same symbols are used for high and low values of k as for m.

The constituents of the R-component are shown graphically, with the scale defined by the distance from the R-corner to base, which represents 100 cation per cent. In routine work a millimeter grid, with a base length of 400 mm and a height of 200 mm is used, here 2 mm = 1 cation per cent.

Fe²⁺ and Fe³⁺ are indicated directly as cation percentages, as shown in Fig. 2.

$Al' = Al - (K + Na) = 22.8 - (2.24 + 4.32) = 15.52$, this distance is marked by a triangular dot downwards from the Fe³⁺.

Each Ca not contained in carbonate may combine with 2 Al of Al' to form anorthite, therefore:

Anorthite-Al = $2(Ca - C)$, limited by the available Al', in the present rock it is $2(6.45 - 1.39) = 10.12$.

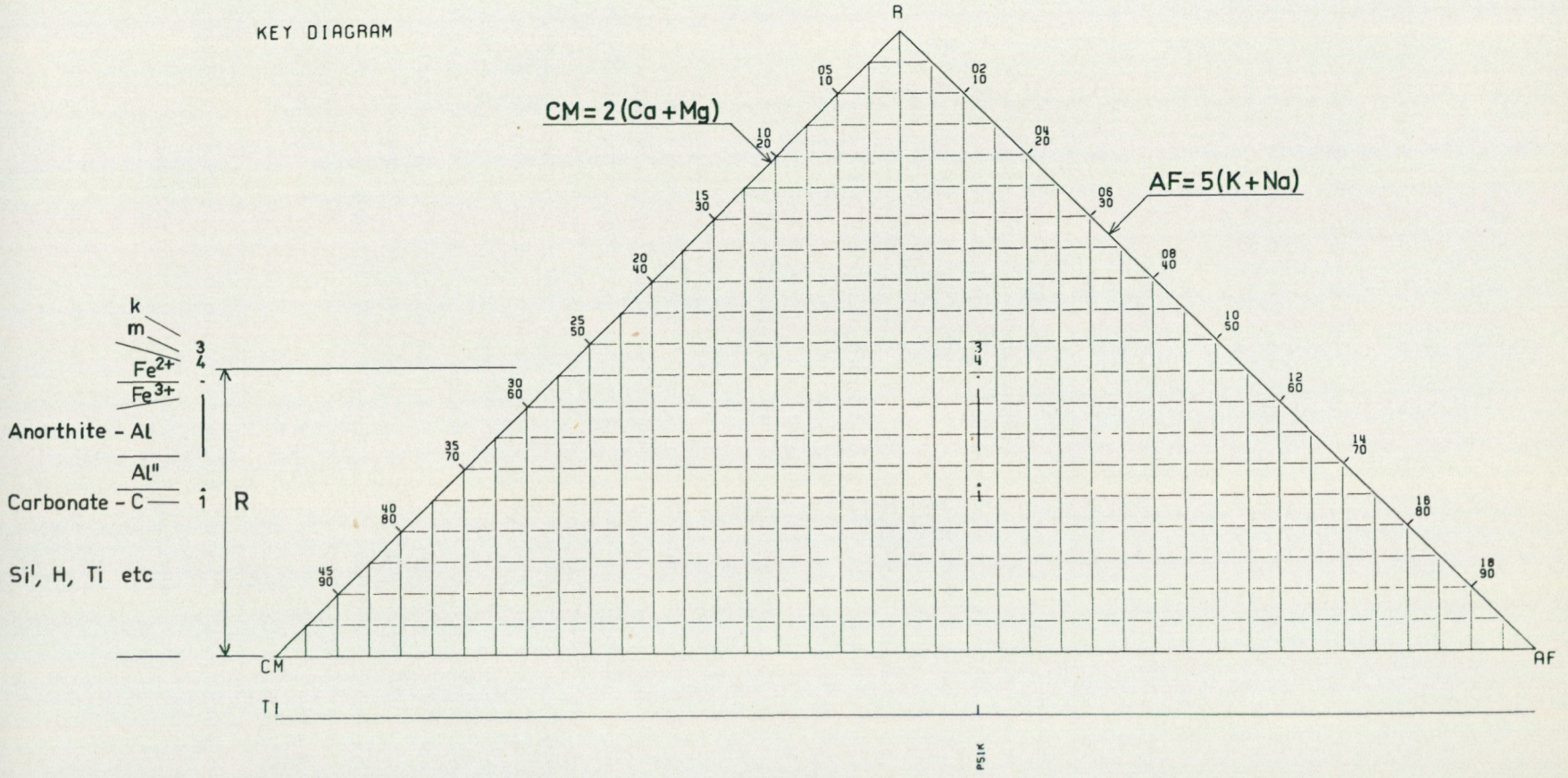
The remaining Al = Al'', which needs no calculation because it is left over when anorthite-Al has been marked in the graph.

Carbonate-carbon = 1.39, it is indicated numerically (1) below the Al' triangular dot. C-contents higher than 9 cation per cent are indicated as follows: A = 10-14 %, B = 15-19 %, C = 20-24 %, D = 25-29 %, E = 30-39 %, F = 40-50 %.

Ti, finally, is shown separately and 2.5 times larger than the other constituents, the distance between the Ti-base and the diagram is equal to 4.0 cation per cent. If Ti exceeds this value it is shown by a dot and using the normal R-scale, in this case the available space permits indication of 10 cation per cent of Ti.

Fig. 2. Key diagram showing the plot of a graywacke, after Pettijohn (1957), cf explanations in the text. This and the following diagrams are made by computer.

KEY DIAGRAM



Some type rocks for background information

By inserting representative compositions of specific rocks in the diagram, a definite background is established, fixing typical positions and indicating systematic trends against which unknown rocks may be judged. To illustrate this a selection of non-metamorphic rocks is shown in Figs. 3-7. No separate listing of the component-coordinates will be given of the individual rocks, because they may be read directly from the graphs. (Such CM:AF coordinates, suitably complemented, might perhaps form the basis of a rational nomenclature of rocks, comparable to the Ab,An-designation of plagioclases). The following general patterns emerging from these plottings may be of interest and help in the diagnosis of rocks:

Normally magmatic suites throughout most of their chemical evolution retain a nearly constant value of R. This as a rule represents less than 50 cation per cent. It also implies that the sum of $\text{CaSiO}_3 + \text{MgSiO}_3 + \text{NaAlSi}_3\text{O}_8 + \text{KAlSi}_3\text{O}_8$ (cation per cent) remains more or less constant during normal magmatic fractionation. Common magmatic trends therefore follow nearly horizontal lines in the lower half of the diagram, reflecting changing CM:AF ratios. This is shown by the rocks of the Cascade, Tahiti and Southern California examples.

High-R suites, such as the batholith of Southern California and the rocks of the Cascade volcanic province, trend towards AF:R ratios near 60:40 in the associated rocks of granitic composition. Minor post- or an-orogenic granites, White Mountain and Arran, in contrast show higher AF:R ratios.

Low-R suites, Tahitian lavas, trend towards feldspathic or feldspathoidal syenitic compositions with still higher AF:R ratios and even negative Si' .

Generalization of this limited evidence might therefore suggest that high R-values identify rock-series of tholeiitic affiliation, and that lower R-values pertain to more alkaline suites. Quartz keratophyres show normal AF:R ratios.

Fig. 3. *Plutonic rocks.*

Batholith of Southern California, from Larsen (1948):

GABBR: San Marcos gabbro (p. 51, 5B).

TONAL: Green Valley tonalite (p. 56, 7A).

TONAL: Bonsall tonalite (p. 66, 8:6).

GRANO: Woodson Mt granodiorite (p. 80, 11:8).

LEUCO: Roblar leucogranite (p. 98, 16).

Arran complex, after Turner & Verhoogen, (1960, p. 337):

A GRA: Granite.

A PIT: Pitchstone.

White Mountain complex, after Turner & Verhoogen, loc cit:

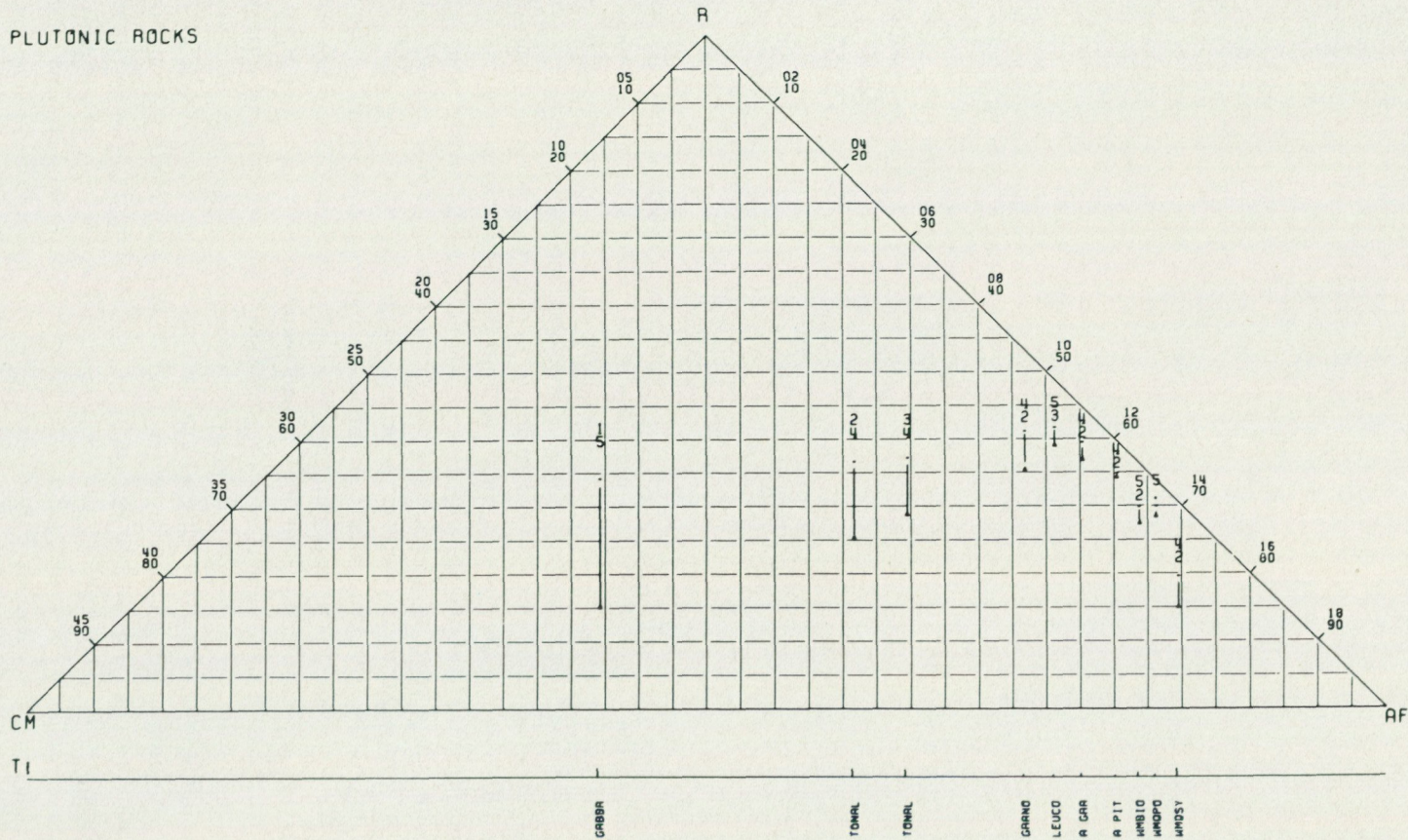
WMBIO: Biotite granite.

WMQPO: Quartz porphyry.

WMQSY: Quartz syenite.

PLUTONIC ROCKS

A GRAPH FOR THE CHEMICAL DIAGNOSIS OF ROCKS



Ultrabasic, anorthositic and other specialized fractionation products are often clearly distinguished by strongly deviating R-values.

Sedimentary rocks generally trend toward the R- and CM (carbonate) corners, and the different groups of sediments occupy different fields in the diagram. The evolutionary series from arkose to high-silica quartzites follows the AF-R side of the triangle, and the corresponding graywacke – subgraywacke – quartzite suite takes a similar course at higher CM- and Fe values. The low maturity and poor sorting of graywackes is revealed by their lower R-values, and the larger horizontal spread in the diagram. This reflects the chemical variation in their sources. Argillitic rocks differ from the graywacke suite by higher Al^{III} and lower anorthite-Al, and from pelites of the graywacke kindred by lower CM-values. The different series of detrital sediments, which are all connected by gradual transitions, generally start from the field of the igneous rocks and converge towards the R-corner. Non-carbonate sediments therefore as a rule show R exceeding 40 cation per cent, but some arkoses may form exceptions. Increasing R in the non-carbonate fraction and increasing carbonate generally signify increasing deviation from the magmatic field and therefore also increasing maturity in the sedimentary products. Formation of authigenic feldspars obviously will give rise to a reversed trend, and others, not discussed here, will result from metasomatism.

Fig. 4. *Volcanic rocks.*

- A. Basalt-Andesite-Rhyolite series, Cascade province, after Turner & Verhoogen, (p. 285):
 OLBAS: Olivine basalt, Medicine Lake.
 OLBAS: Olivine basalt, Newberry.
 OLBAS: Olivine basalt, Outerson Mt.
 BSAND: Basaltic andesite, Crater Lake.
 HYAND: Hypersthene andesite, Crater Lake.
 PYAND: Pyroxene andesite, Mt St Helens.
 PODAC: Porphyrite dacite, Medicine Lake.
 DACIT: Dacite, Crater Lake.
 RHYOL: Rhyolite obsidian, Newberry.
 RHYOL: Rhyolite, Medicine Lake.
- B. Alkaline olivine-basalt association, Tahitian lavas, after Turner & Verhoogen (p. 187):
 ANKAR: Ankaramite, average.
 BASAN: Basanitoid, average.
 TAHIT: Tahitite, average.
 PHON: Phonolite, average.
 PHTRA: Phonolite trachyte, average.
 The low-R Tahitian trend is marked by a broken line.
- C. Keratophyres, Turner & Verhoogen (p. 262):
 QKER: Quartz keratophyre, Great King Island.
 QKER: Quartz keratophyre, Eastern Oregon.
 MAGKE: Magnetite Keratophyre, Nundle.

VOLCANIC ROCKS

A GRAPH FOR THE CHEMICAL DIAGNOSIS OF ROCKS

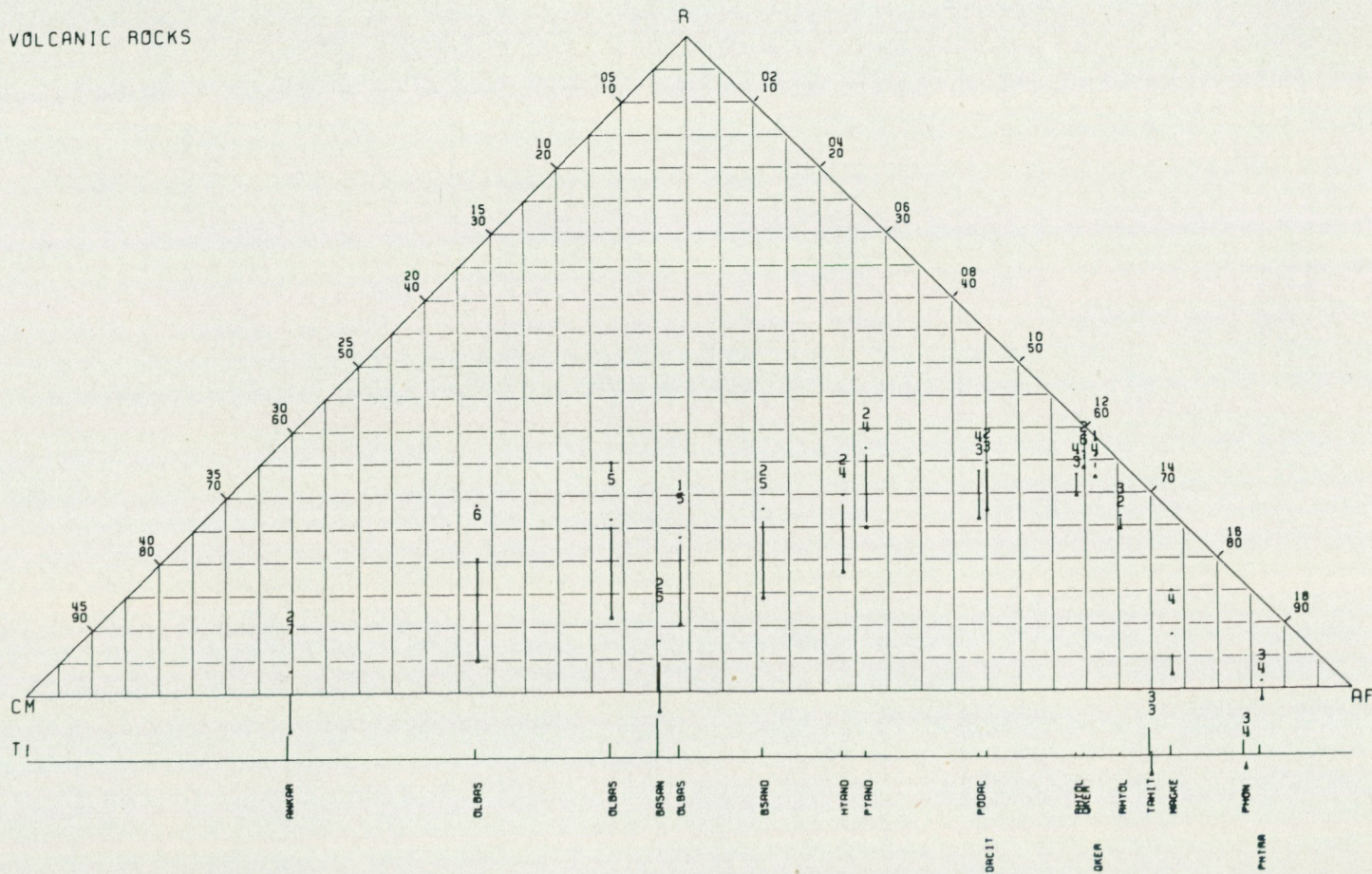


Fig. 5. Sedimentary rocks I, arkoses and other sandstones.

Arkoses from Pettijohn (1957, table 56, p. 324):

P56A Portland stone, Conn.

P56B Torridon sandstone, Scotland.

P56C Torridon arkose, Scotland.

P56D Lower Old Red sandstone, Scotland

P56E Sparagmite, Norway

P56C in its composition approaches the "acid" graywackes, cf Fig. 6.

Subgraywackes and protoquartzite, from Pettijohn (1957, table 54, p. 319):

P54A Subgraywacke from Stanley shale, Arkansas

P54B Subgraywacke from Tyler slate, Wisconsin

P54C Frio sandstone, aver., Texas. Chemically a subgraywacke displaced toward the CM-corner by its content of calcite.

P54D "Graywacke" phase, Minnesota

P54E Berea protoquartzite

Fig. 6. Sedimentary rocks II, graywackes, from Pettijohn (1957, table 51, p. 306):

P51A Paleozoic, New Zealand

P51B Trias - Jura, New Zealand

P51C Archean, Minnesota

P51D Archean, Ontario

P51E Franciscan, California

P51F Archean, Ontario

P51G Eocene, Washington

P51H Keewatin, Ontario

P51I Kulm, Germany

P51J Rensselaer, New York

P51K Aure, Papua

P51L Cretaceous, Papua

P51M Tanner, upper Devonian - lower Carboniferous.

These rocks show considerable variation:

P51K is highly immature and approximates a basaltic composition, only Al³⁺ indicates the effects of hydrolysis (exogene).

P51L, F, D and H are markedly argillaceous, L might also be classed as an argillaceous sub-graywacke, cf P54A, Fig. 5.

P51J, I and E indicate acid or intermediate source rocks, whereas the others seem to derive from more basic terrains.

Fig. 7. Sedimentary rocks III, shales and marls.

Silurian pelites of the Scandinavian Caledonides, after Vogt, from Miyashiro & Haramura (1966, p. 46):

56. Western facies (pelites of graywacke kindred, cf 66).

57. Eastern facies (argillites).

Paleozoic pelites of Japan, from Miyashiro & Haramura, loc. cit., table III:

58. Northern zone.

59. Northern Kiso area.

60. Dando area, Ryoike - Abukuma metamorphic belt.

63. Bessi area, Sanbagawa metamorphic belt.

65. Southern zone.

66. Hitati facies (graywacke kindred).

Marly sediments, from Niggli (1952, p. 312, 313):

67, 69, 70, 71, table 50, analyses nr 43, 45, 46, 47.

72, table 49, analysis nr 35.

Siliceous shales, from Pettijohn (1957, p. 324):

85-87, table 71, A-C.

GRAYWACKES AND OTHER SANDSTONES

R

05
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02
10

10
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04
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CM

AF

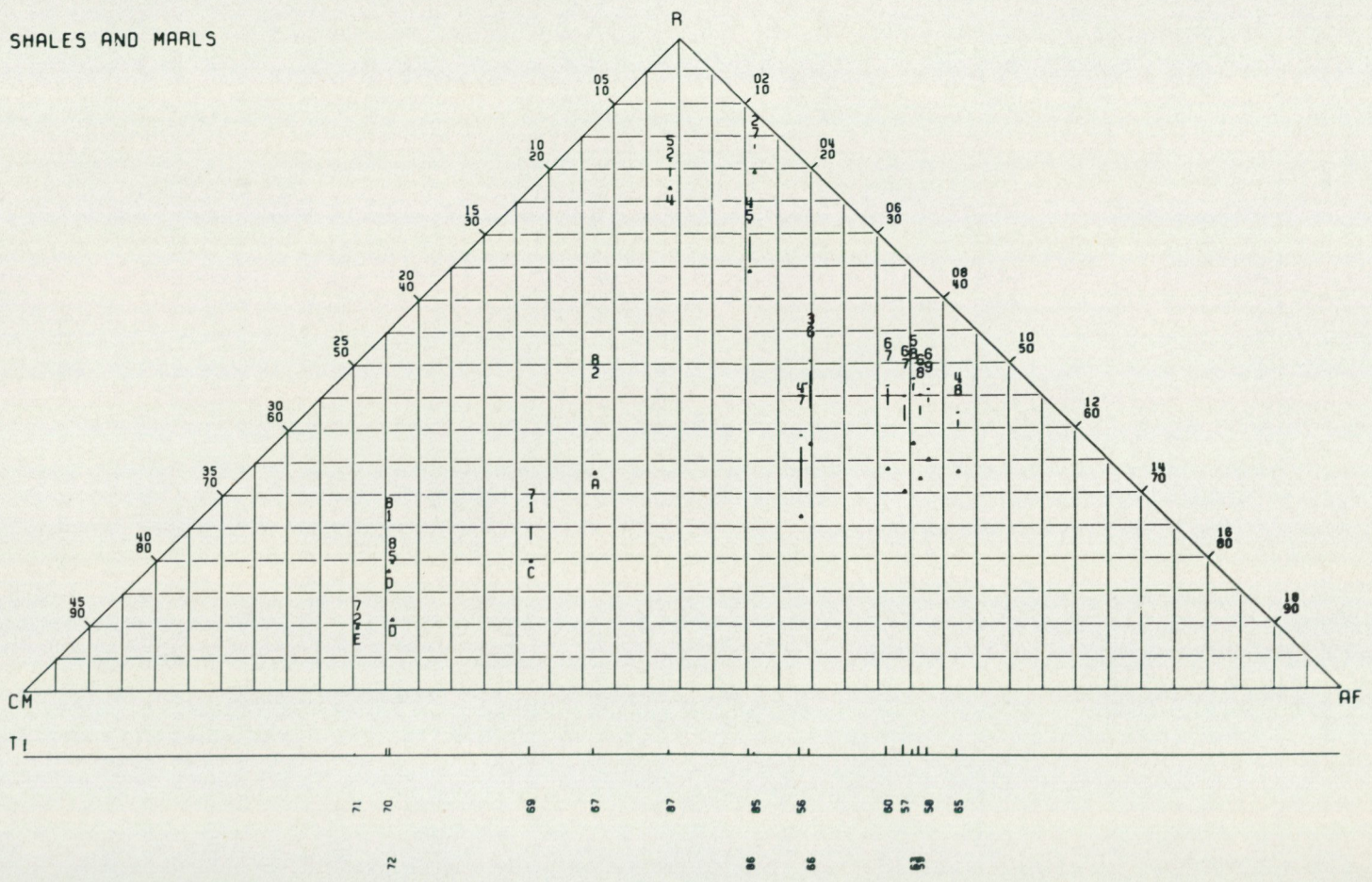
T1

PS1K
PS1L
PS1C
PS1G
PS1B
PS1A
PS1D
PS1J
PS1I
PS1E

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SHALES AND MARLS

A GRAPH FOR THE CHEMICAL DIAGNOSIS OF ROCKS



Some rules for diagnosis

These examples, together with common petrological knowledge, suggest the following rules for diagnosis. They must in each case be supplemented by special consideration of the other quantities and ratios shown in the diagram.

High AF and/or high a northite-Al, Al'' being low or missing, often indicates unweathered igneous rocks; high CM here characterizes the more basic rocks.

High CM with Ca higher than or equal to Mg often indicates the original presence of a distinct carbonate fraction, even if CO₂ has been later lost in metamorphism.

High CM with predominant Mg and variable Fe but low R characterizes ultrabasic rocks. Final diagnosis often depends on high contents of Ni and Cr among the trace constituents.

High CM combined with high R, notably Al'', would characterize restite rocks, which develop from pelites by anatectic formation of granitic rocks.

High R signifies sediments of the resistate (Si'), hydrolysate (clay-Al''), oxydate (ferric iron) and redusate (ferrous iron) groups, cf. Goldschmidt (1934), as well as cherty matter (Si') and many products of hydrothermal alteration.

Low R in silicate rocks indicates the presence of feldspathoids, olivine, or other minerals less siliceous than feldspars and pyroxenes. Such rocks may plot outside the triangular diagram, indicating formally a negative R. In this respect the present graph corresponds to the Px-Q-Fl diagram, for which the same feature has been elaborated by Barth (1955).

Examples of diagnosis

The purpose of the following examples is to demonstrate the application of this graph to metamorphic rocks.

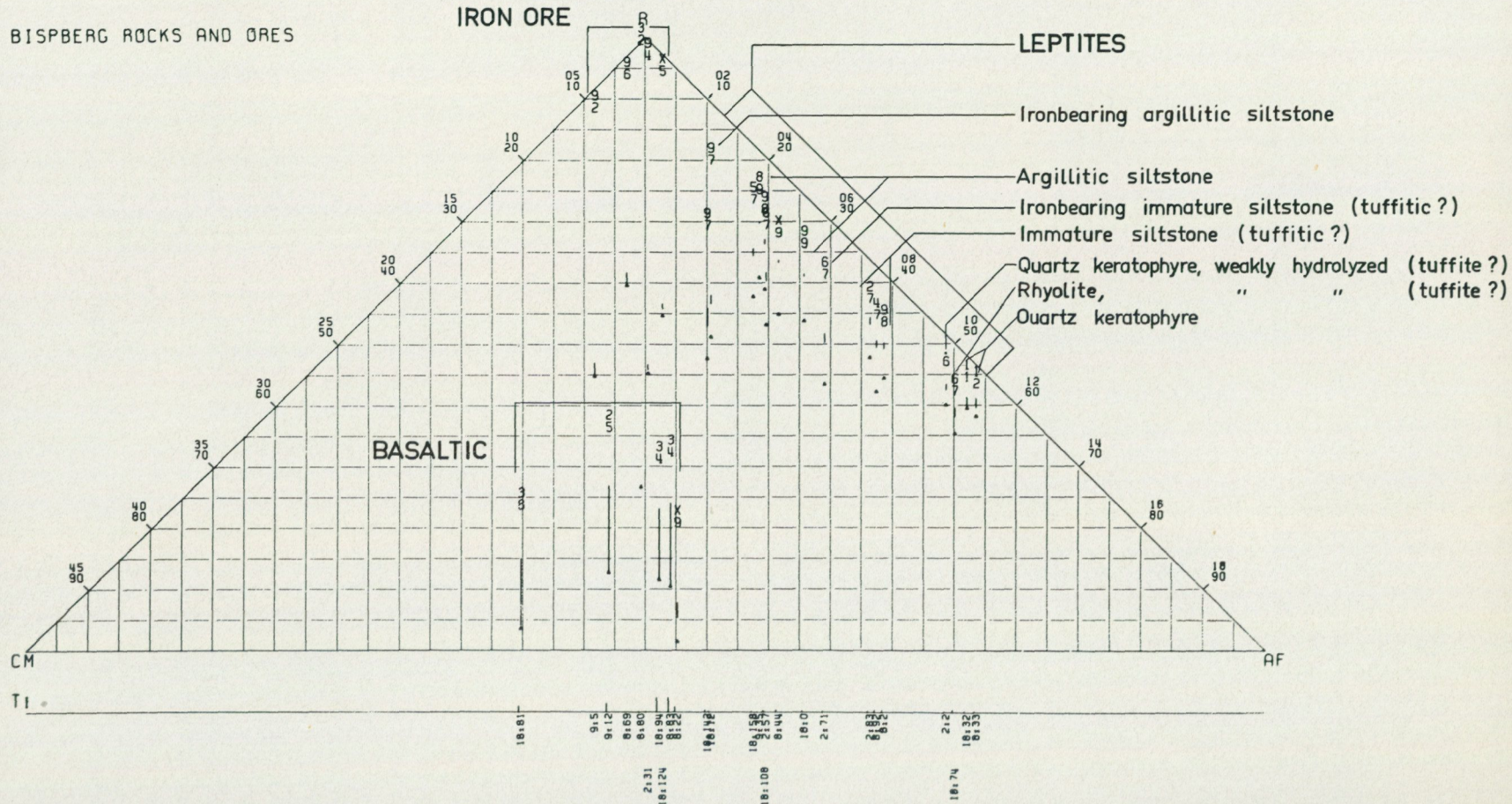
Fig. 8 shows 26 compositions of rocks and ores of the Bispberg mines, a deposit of quartzbanded iron ore in central Sweden. Each composition represents one 10 cm sample of drillcore only. A distinct grouping into ores, meta-basaltic rocks and leptites can be seen. Obviously the leptitic rocks form no distinct cluster but fall into a neat and narrow row, which suggests rather continuous

Fig. 8. Rocks and ores of the Bispberg Mine, with tentative diagnosis of the premetamorphic nature of the leptitic rocks. Sample 8:22 by its high k- and m-values and its Al'' content differs from the truly basaltic rocks.

BISPBERG ROCKS AND ORES

IRON ORE

LEPTITES



transition from igneous compositions high in AF, notably albite, to sedimentary ones, high in R and Al". The igneous compositions correspond closely to the quartz-keratophyres of Fig. 4. Corroborating evidence is provided by Table 1 below, which shows the composition of some "end members" of this leptite series, and some non-metamorphic rocks selected for comparison by geochemical ranking after O. Brotzen, loc.cit. In conclusion the leptites of Bispsberg apparently represent a series of mixed volcanic - sedimentary origin, comprising acid volcanics of the quartz keratophyre type and all transitions to fairly typical sediments, comparable to Mississippi delta sediments. Their compositions are not typical of sandstones or argillites, as represented in Fig. 4, but take an intermediate position, corresponding to argillitic silt- and mudstones, which is in harmony with their present fine-grained metamorphic textures. In principle the series of leptites may also be interpreted as a product of progressive argillitic alteration of the volcanic members, considering the geochemical similarity of exogenic and hydrothermal hydrolysis. Regardless of interpretation this example illustrates the significance of the composite AF- and R-components, although their constituent elements show little or no internal correlation. The rather continuous series of the leptites, showing no marked clustering but indicating a gradual change, would not have been recognized if potassium and sodium had been taken as separate dimensions.

Table 1
(weight per cent)

	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O
1	77.3	0.16	12.8	2.4	0.8	0.12	5.8	0.5
2	75.1	0.22	12.8	2.3	0.3	0.30	5.1	2.4
3	75.0	0.10	13.4	2.1	0.4	0.18	6.4	0.8
4	75.2	0.12	11.0	5.6	0.4	1.3	0.3	3.3
5	71.6	0.11	11.7	9.4	0.7	1.5	1.2	2.3
6	71.5	0.59	10.6	3.5	0.5	1.4	1.5	2.3

1. Leptite, Bispsberg, V 8:33.8 m.

2 & 3. Quartz keratophyres from Turner & Verhoogen (1960) p 262.

4. Leptite, Bispsberg, V 18:108.0 m.

5. " V 2:57.2 m.

6. Mississippi mud minus Ca CO₃, from Niggli (1952) p 308.

4 & 5 carry a slight dissemination of iron oxides.

Fe₂O₃ stands for total iron oxides.

GNEISSES OF THE STOCKHOLM REGION

Next two groups of gneisses from the Stockholm region, recently described by Stålhös (1969), will be considered, cf. Figs. 9, 10. Preliminary inspection suggests that the garnet-bearing veined gneisses of Fig. 9 by their homogeneous distribu-

VEINED GARNET GNEISSES, STOCKHOLM

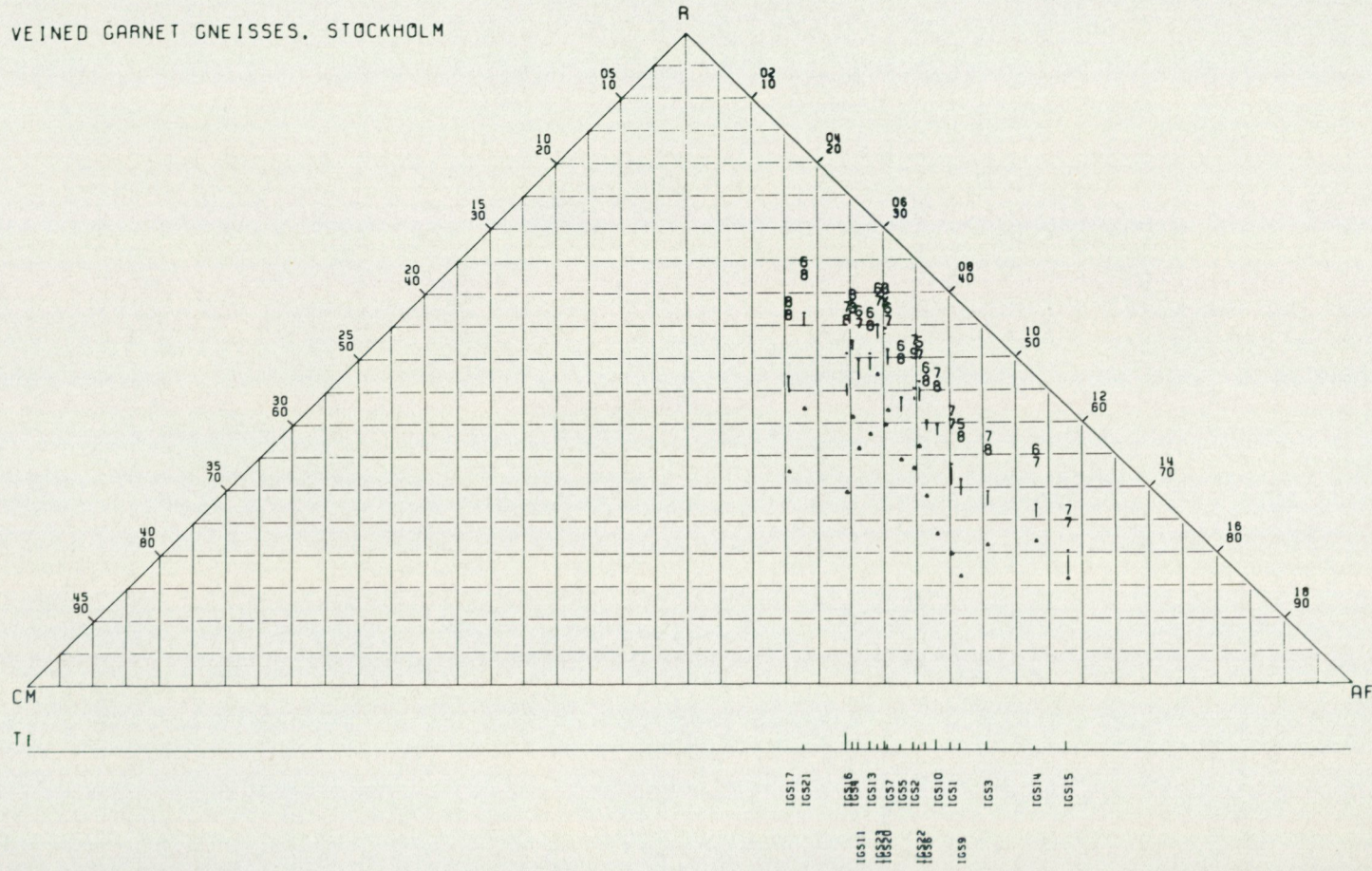


Fig. 9. Veined garnet-bearing gneisses from the Stockholm region, from Stålhös (1969, Table 1).

tion, high Al'' and very obvious sedimentary trend towards the R-corner, represent metamorphic equivalents of a coherent group of sediments, reflecting strong chemical weathering or comparable decomposition. A distinctly complex distribution is in contrast shown by the gray gneisses from the same area, cf. Fig. 10, which are split into four sets, each with separate, welldefined R- and AF values. These gneisses appear to represent no single type of rock. All of them by their relatively low R and subordinate Al'' indicate rather limited chemical weathering. They therefore resemble igneous rocks as well as immature sediments.

Comparison of the garnet-bearing group with Fig. 7 indicates that these gneisses represent argillitic sediments, as already stated by Stålhös (*loc.cit.*). The maturity of these rocks must have been remarkably high, in many cases exceeding that of the comparable samples in Fig. 7, (nos. 57-65). No radical metasomatism is reflected in the diagram, Fig. 9, except samples 1GS14 and 1GS15, which may show evidence of feldspathisation. It is interesting to note that no variational trend towards or away from the composition of granite, (at AF60, R40, cf. Fig. 3), can be observed. This means that granitic matter has not been added to or extracted from these veined gneisses.

Regarding the gray gneisses, Fig. 10, it is seen that sample 9GS2 represents a basaltic rock, with definite evidence of alteration in its high k-value. Samples 9GS8, 6GS4, 7GS1, 7GS2 and 6GS7 represent typical graywackes, whereas samples 6GS5, 6GS2, 6GS3, 6GS6 and 6GS1, marked by reduced CM and anorthite-Al, show effects of stronger sorting, and are better classed with the subgraywackes.

Finally, the three remaining compositions, 7GS3,-4,-5, with their separate position, high AF- and low R-values, more likely represent metamorphic dacitic and rhyodacitic rocks, which apart from being more sodic, bear a strong general chemical resemblance to the dacites of the Cascade province, cf Fig. 4.

There may be little cause to press this point further and to argue at length whether these highly metamorphic samples represent truly volcanic rocks. As is shown by the example of the Bispberg leptites there exists no clearcut division between volcanics and immature detrital sediments. The geologically essential point is that the Stockholm gneisses can be shown to derive from highly mature argillitic sediments along with typical graywackes and rocks which indicate the presence of rather fresh volcanics of the daciterhyolite kindred, either within the gneiss-sequence or in nearby source areas.

Technically, the example of the gray gneisses illustrates the direct genetical significance pertaining to the position of individual compositions in the graph. The case of the veined, garnet-bearing gneisses shows the diagnostic value of representing quantitatively total composition, whereby rectilinear relations of addition and subtraction exist in the diagram.

GREY GNEISSES, STOCKHOLM

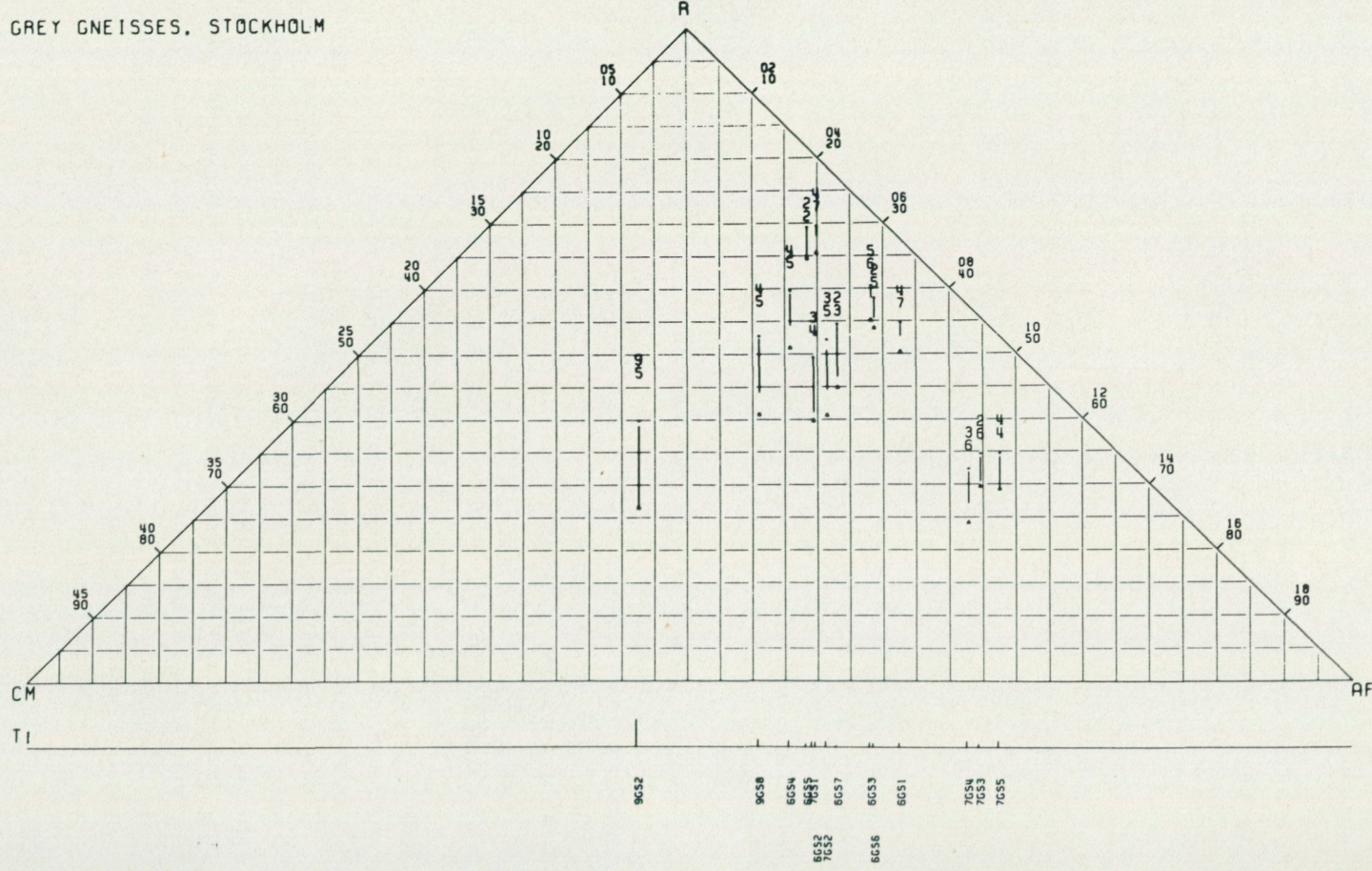


Fig. 10. Gray gneisses from the Stockholm region, after Stålhös, loc. cit., tables 6, 7, and 9.

KIRUNA GREENSTONES AND PORPHYRITES

These rocks have been studied since the begin of this century and a recent summary has been given by Offerberg (1967). The greenstones and porphyrites are clearly igneous, predominantly basic rocks and comprise effusive as well as some intrusive members. They form a conspicuous part of the pre-Cambrian complex surrounding the famous Kiruna iron ore deposit. Their stratigraphical relations as well as their petrographic subdivision and classification are still to some extent problematical. A remarkable feature of these rocks is their richness in albite, and the same feature also characterizes the felsic porphyries with which the iron ores are associated. It early attracted special attention, cf. Geijer (1916) and Sundius (1916), which finally led to the well-known study on spilitic rocks by Sundius (1930). Since that time many new analyses of the Kiruna rocks have become available. They are listed by Offerberg, loc.cit. According to his account of the geological occurrence and regional distribution of the rocks, they can be subdivided into the following three sub-groups:

A. The Kiruna greenstones sensu stricto are found west of Kiruna as a series of more or less metamorphic basic rocks, largely made up of amygdaloidal flows and of pillow lavas, in places resting on an old granitic basement with its cover of quartzite and carbonate sediments. The greenstones themselves are in turn overlain by a series of metamorphic detrital sediments followed by the Kiruna porphyries.

B. The Kiruna porphyrites underlie the Kiruna porphyries just like the greenstones. They are found to the south of Kiruna, and their relations to the greenstones cannot be satisfactorily established. Rocks very similar to the Kiruna greenstones are, however, found within the porphyrites, usually in the upper part of the porphyrite sections. The basis of the porphyrite series is unknown.

C. The basic members of the Kiruna porphyries occur intercalated in the predominantly felsic series of the latter rocks and in their basal zone against the porphyrites.

Finally there occurs in the region a fourth group of greenstones, the Paitsjärvi group, which shows great similarity to the Kiruna greenstones, although resting with a basal conglomerate upon the Kiruna porphyries. Unfortunately there exist no analyses of the Paitsjärvi rocks.

All available compositions are plotted in Fig. 11. Evidently this graph is dominated by a more or less horizontal trend, thereby differing from the previous ones, and reflecting the typical igneous trend from high CM to high AF at constant R, discussed at the outset. A certain clustering is suggested by the diagram.

Comparison of Fig. 11 with the volcanics in Fig. 4 brings out a number of interesting features:

KIRUNA GREENSTONES AND PORPHYRITES

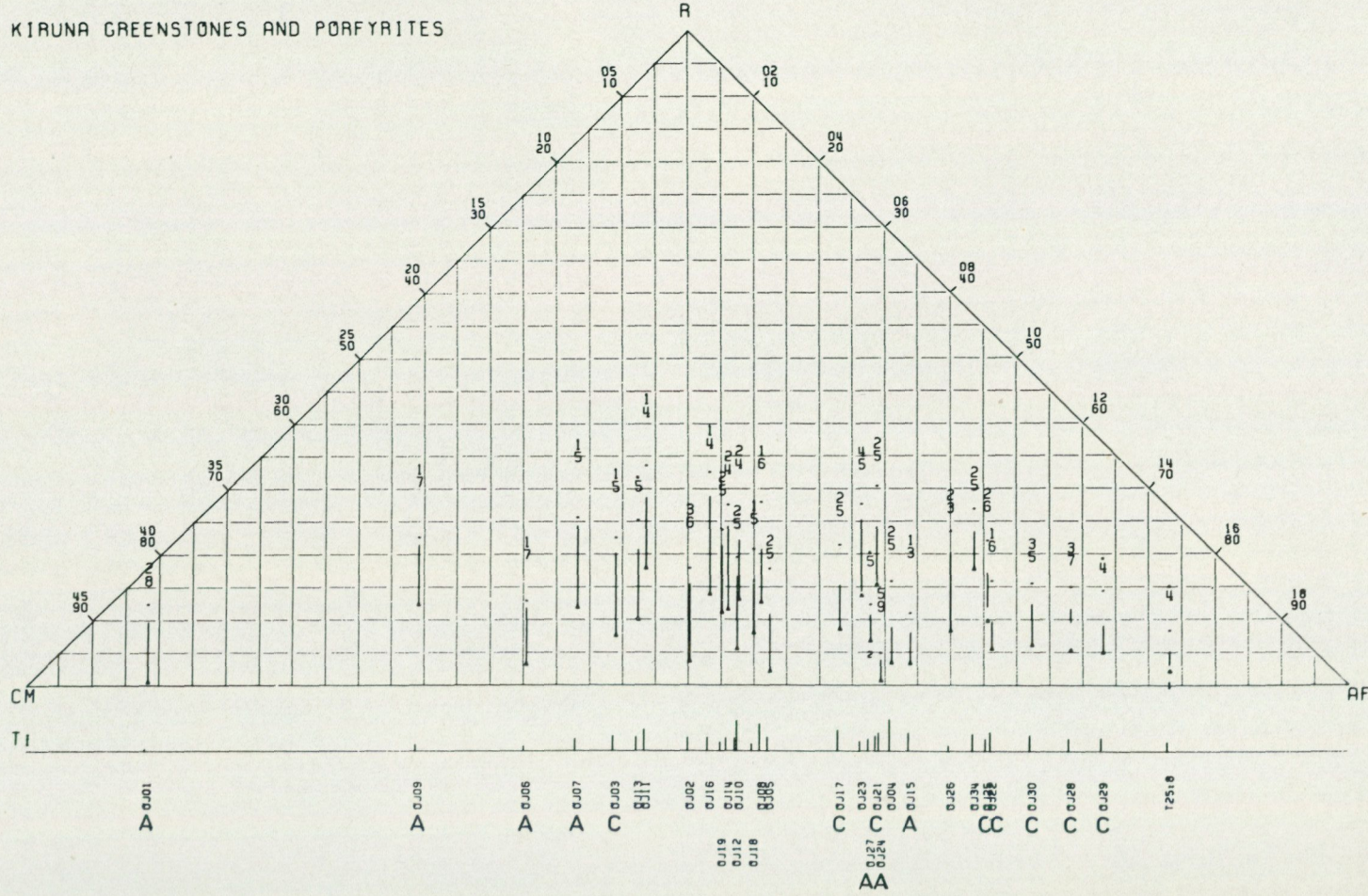


Fig. 11. Composite group of effusive Kiruna greenstones, from Offerberg (1967).

A - Kiruna greenstones, ss.

C - Basic members of the Kiruna porphyries.

Unmarked - Kiruna porphyrites.

T25:8 - Magnetite keratophyre from Nundle, New South Wales, cf Fig. 4.

The composite group of Kiruna rocks has a remarkable horizontal spread, indicating a range of fractionation comparable to that of the volcanics of the Cascade province and of Tahiti. In their general trend and spread of R-values the Kiruna rocks obviously take an intermediate position between these two type-series of volcanic rocks. In the diagram it is clearly seen, however, that they are characteristically different from the other volcanics in one respect - the iron content. In the Kiruna rocks the cation percentage of iron remains approximately constant throughout the entire fractionation range, whereas the Cascade and Tahiti volcanics show a systematically decreasing iron-content with decreasing CM:AF ratios. It may be suggested that this distinctive mark of the Kiruna rocks is a lithochemically significant feature of this important iron-ore province in northernmost Sweden.

The three subgroups of the Kiruna greenstones are also seen in Fig. 11 to have somewhat differing distributional fields, although they all comprise rocks of nearly identical basaltic composition, e.g. samples 13, 32 and 3. These three compositions seem to mark the starting point of fractionation towards higher AF values, and therefore may be inferred, after Nockolds and Allen (1953) to represent the parental magmas. Compositions are given in Table 2.

Table 2 (weight per cent)

	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O
3	47.4	1.37	16.8	3.42	8.45	7.9	9.3	2.8	0.7
13	50.2	1.24	15.4	6.27	5.34	6.3	10.6	3.3	0.2
32	48.6	1.13	13.5	3.56	10.2	7.4	8.6	2.9	0.3
A	48.7	1.25	15.2		12.4	7.2	9.5	3.0	0.4
B	50.7	1.30	14.3		12.0	6.9	8.6	2.9	0.7
C	47.1	2.9	15.8		12.3	7.4	9.4	3.1	1.3
29	55.8	1.18	17.0	7.35	3.42	1.44	2.93	7.7	0.5
D	56.95	.89	17.9	4.49	6.0	.93	2.30	8.8	0.4

3, 13, 32; basaltic greenstones, Kiruna, after Offerberg, loc.cit.

A. Average of these three compositions.

B. " 8 New Jersey basalts, Turner & Verhoogen, 1960, p. 208.

C. Average olivine basalt, Carboniferous of Scotland, from Turner & Verhoogen, loc.cit., p. 192.

29. Andesitic greenstone, Kiruna, after Offerberg, loc.cit.

D. Magnetite keratophyre, Nundle, from Turner & Verhoogen, 1960, p. 262. Also contains 0.91% CO₂.

B, C and D selected by geochemical ranking.

It can further be noted in Fig. 11 that the porphyrites (subgroup B), form a set with a more limited fractionation range, and characterized by the prevalence of relatively high R-values, indicating a more tholeiitic nature. The Kiruna greenstones, *sensu stricto* (subgroup A) in contrast show an extensive fractiona-

tion range, with low R-values and a notable participation of basic and ultrabasic differentiates with high CM:AF ratios. Finally the basic members of the Kiruna porphyries (subgroup C) form an extensive series towards high AF-values and with R-values decreasing slightly in this direction.

It can also be concluded from Fig. 11 that the soda-rich nature of these rocks must be an original feature and can not be due to an addition of albite. Such an addition would have given rise to a compositional trend directed straightly towards the AF corner. Likewise the albite is not due to alkali-metasomatism affecting normal, more anorthite-rich, rocks, for the Mg:Ca ratios are fairly constant throughout the entire AF-range and the contents of anorthite-Al have not been reduced by transformation to alkali feldspar. A single good case of alkali-metasomatism is found in sample nr 24. This can be seen from its high Mg:Ca ($m = 9$) and K:Na ($k = 5$) ratios as well as the reduced content of anorthite-Al. Here petrographic signs of alteration are also reported by Offerberg, loc.cit. Sample 28 shows signs of hydrothermal alteration or weathering, with a notable Al³⁺-content and $m = 7$. It can finally be seen that the greenstones of subgroup C, rather than bearing signs of general albitization or alkali-metasomatism, show a clear fractionation trend towards the composition of the magnetite keratophyre of Fig. 4, which has been inserted in Fig. 11. This is further corroborated by the data of Table 2.

All these observations, the singular fractionation trend, the undisturbed Mg:Ca ratios and the normal contents of anorthite-Al, very clearly point to the conclusion, that the high soda content of these rocks is predominantly a primary feature, and that the long reported observations of albite replacing more calcic plagioclases most probably reflect the adjustment of the plagioclases to the present epidote- and hornblende-bearing condition of the rocks. This was at an early date noted by Sundius (1916), but has been questioned by many other workers. To complete the picture of these sodic greenstones it may finally be mentioned that they are not associated with any thick sequence of graywacke sediments.

Technically this example shows the value of breaking down the composite CM-, AF- and R-components into separate constituents, and the diagnostic value of those chosen in the present graph.

Discussion and general conclusions

The examples given show that the present graph, like so many others, can be used to illustrate common chemical trends of magmatic fractionation. In addition it can be applied to sedimentary rocks, where earlier work by Poldervaart and Green (1958) has demonstrated the inefficiency of a number of

diagrams. Combination of these two objectives into one diagram often makes possible the chemical diagnosis of rocks of uncertain origin even if only a single analysis is available and direct inspection of the chemical and mineralogical composition appears inconclusive.

It has also been shown that relating observed variational trends to the familiar effects of igneous and sedimentary fractionation makes possible the recognition and testing of effects of other less well-known processes, suspected or real. The veined, garnet-bearing gneisses of the Stockholm region and the Kiruna greenstones illustrate this. The fact that no trend towards or away from granitic compositions is superposed upon the sedimentary trend displayed by the veined Stockholm gneisses shows that suspected injection or segregation of granitic matter has been rather insignificant, and that the mobility of granitic vein-material has been restricted. Here straightforward demonstration of similarity between the average composition of the gneisses and that of less metamorphic pelites would be inconclusive. An unchanged average composition could not rule out migration of anatectic vein-material within the gneiss complex, but such migration would be clearly revealed as a special trend in the graph, because the vein-material would have been added to some samples and subtracted from others.

The plotting of the Kiruna greenstones apart from showing their general magmatic trend also revealed that iron remained practically constant throughout fractionation. It further permitted diagnosis, in the negative, on the role of albitization and alkali-metasomatism in these rocks.

Basically this wide applicability is achieved through three principal features of the diagram:

1. By showing total composition rather than any selected number of components different changes in the samples can be noted, rectilinear relations of addition and subtraction are retained, and no misleading confusion of relative proportions and true percentages can arise. This feature also avoids restricting variability by tying it to one particular component or group of components.

2. The selection of petrologically significant componental groups, as discussed in the section on principles, also is fundamental to diagnosis. The present diagram therefore differs from the conventional QLM-triangles and the Px-Q-FI diagram of Barth, *loc.cit.*, by separating anorthite from the alkali-feldspars, separating excess alumina from L and Px respectively, and by isolating iron and treating it as a separate component of the R-group. This latter feature leaves many lithochemical trends unaffected by the complexities which pertain to iron in magmatic fractionation, and at the same time permits direct study of the specific variations of this element.

3. Separate presentation of the individual constituents of the composite components likewise is instrumental in diagnosis with this graph, as was shown

in the discussion of the Kiruna greenstones. This feature permits simultaneous observation of all individual changes in relation to total change, although the complexity introduced hereby is no greater than that required for showing individual elements in common types of composite variation diagrams.

The last two aspects, relating to the selection of components and of component groups are probably valid also for development of more refined computerized models. The examples given, as well as general petrological experience, suggests that the ability of individual elements to enter different functional combinations must be given adequate expression. For instance, in the present graph Al for proper representation is divided between three such functional units, namely the alkali-feldspars, anorthite-Al, and Al³⁺. Computers could pursue this differentiation to the point where rock composition is stated in terms of actual minerals, but this again might obscure valid trends in lithochemical fractionation. Indeed study of the present graph suggests that more complex models, which permit separate representation of all individual components or minerals, would require a superstructure which makes possible proper evaluation of the joint variation of those geochemically vicarious or coherent components, which in the triangular diagram are combined in the CM-, AF- and R-groups respectively.

Regarding the number of rock-compositions which can be represented in the suggested diagram some comment may also be justified. It is, of course, dependent on the distributional range of the rocks, as well as the scale of the diagram. Fig. 11, for instance, contains 31 individual compositions, and twice this number has been accommodated in a diagram showing a more varied assemblage of rocks. It should be pointed out, however, that separate representation of the constituents of the R-component as vertical bars does not impair markedly the capacity of the diagram. Most variations in rocks affect the CM:AF ratio, thereby resulting in some horizontal displacement of rock-locations. Therefore the present capacity is sufficient for many phases of normal geological work. For investigations of larger rock-populations contour-lines indicating point densities in the diagram offer considerable promise. It is thus possible to combine the present diagram with a computer program which calculates and memorizes very great numbers of individual markings in the graph, and which prints out maps of point densities for the different parameters. This finally stresses the most distinct advantage of graphical representation, namely the resulting direct visualization of many lithochemical features. Often this leads to recognition of critical variables, which can subsequently be investigated numerically or be more clearly illustrated by rearrangement into other diagrams. In this respect the present graph may perhaps be of a more general petrological interest. Its prime function is, however, to serve as a general purpose diagram by providing a basic and uniform technique for the diagnosis and illustration of the chemical nature of different common rocks.

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GFF = Geol. Fören. Stockholm Förh.

SGU = Sveriges Geol. Unders.

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